"New Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells"
Quarterly Report for 3/31/2006 to 6/30/2006

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Abstract

Operation of SOFCs at intermediate temperatures (500 – 800 ºC) requires new combinations of electrolyte and electrode materials that will provide both rapid ion transport across the electrolyte and electrode - electrolyte interfaces and efficient electrocatalysis of the oxygen reduction and fuel oxidation reactions. This project concentrates on materials and issues associated with cathode performance that are known to become limiting factors as the operating temperature is reduced.

The specific objectives of the proposed research are to develop cathode materials that meet the electrode performance targets of 1.0 W/cm^2 at 0.7 V in combination with YSZ at 700 ºC and with GDC, LSGM or bismuth oxide based electrolytes at 600 ºC. The performance targets imply an area specific resistance of ~0.5 Ωcm^2 for the total cell. The research strategy is to investigate both established classes of materials and new candidates as cathodes, to determine fundamental performance parameters such as bulk diffusion, surface reactivity and interfacial transfer, and to couple these parameters to performance in single cell tests.

In this report, further measurements of the oxygen deficient double perovskite $PrBaCo_2O_{5.5+\delta}$ are reported. The high electronic conductivity and rapid diffusion and surface exchange kinetics of PBCO suggest its application as cathode material in intermediate temperature solid oxide fuel cells. Preliminary measurements in symmetric cells have shown low ASR values at 600 °C. Here we describe the first complete cell measurements on Ni/CGO/CGO/PBCO/CGO cells.

Table of Contents

1. List of Graphical Materials

2. Introduction

The objectives of the project are to discover new oxide cathode materials that meet a performance target of 1.0 W/cm^2 at 0.7 V in combination with YSZ at 700 ºC and with CGO, LSGM electrolytes at 600 ºC. An ancillary objective of the project is to increase fundamental understanding of the intrinsic transport properties of mixed electronic ionic conducting oxides and oxide-oxide interfaces that can be used to accelerate further progress in the development of cost effective high performance solid oxide fuel cells. In Phase I, we are measuring the surface exchange rates, diffusion coefficients and interfacial transport for an initial set of perovskite related oxide materials. In Phase II we will synthesize and characterize new cathode materials and measure their kinetic parameters. The thermal and chemical compatibility with different electrolytes will be determined. Based on the results, a subset of the best materials will be selected for single cell tests. The phase III objectives are to evaluate the performance of the best materials identified in Phase I and II. The optimum electrode composition and microstructure will be determined and the longer term performance characteristics evaluated.

3. Executive Summary

The project began on October 1, 2003 and this is the eleventh quarterly report. The high electronic conductivity and rapid diffusion and surface exchange kinetics of the oxygen deficient double perovskite $PrBaCo_2O_{5.5+\delta}$ (PBCO) suggest its application as cathode material in intermediate temperature solid oxide fuel cells. In the previous report, we described measurements on symmetric cells with PBCO electrodes and demonstrated that low ASR values could be obtained at 600 °C. In the present work we have extended these measurements to complete cells and describe the results that we have obtained for electrolyte supported cells.

4. Experimental

4.1 Sample preparation

The CGO (gadolinium doped ceria) powder was die-pressed into a pellet and sintered at 1450°C for 8 h in air. The thickness of the CGO electrolyte pellet was reduced to 0.8 mm by polishing with SiC paper. $PrBaCo_2O_{5+x}$ (PBCO) -CGO (50 wt%) was used as the cathode and Ni-CGO (30 vol%) as the anode, respectively. The PBCO-CGO and NiO-CGO pastes were prepared from powder mixtures of PBCO and CGO, NiO and CGO, with the addition of terpineol. The NiO-CGO paste was applied onto the CGO electrolyte and fired at 1300°C for 2 h in air. Then a thin PBCO-CGO green tape (25 μm), which was prepared by tape casting, was stuck to the other side of the CGO electrolyte pellet using terpineol and fired at 1100°C for 30 min in air. The PBCO-CGO paste was subsequently applied onto the surface of the sintered PBCO-CGO tape, and also fired at 1100°C for another 2 h in air to increase the thickness of the cathode. The active electrode area of the cathode and anode was 1.27 cm^2. Two pieces of gold mesh were used as current collectors and bonded onto both surfaces of the cathode and anode by firing with gold paste at 700°C for 30 min in air.

4.2 Electrical measurements

An electrolyte supported solid oxide fuel cell with the following arrangement was tested from 500°C to 700°C at 25°C intervals.

97 vol% H_2 + 3 vol% H_2O, Ni-CGO anode / CGO electrolyte / PBCO-CGO cathode, air

The anode side of the single cell was sealed onto an alumina tube with a gold O-ring under spring loading, while the cathode was simply exposed to air. Before testing, the cell was heated to 800 °C to deform the gold O-ring and reduce the NiO to Ni with hydrogen flowing over the anode. The flow rate of the hydrogen fed to the anode was 150 cc/min. Cell current-voltage (I-V) plots were measured using an Arbin Testing System (Model BT 4+). The ohmic resistance of the cell was determined by current interrupt measurements using Keithley SourceMeters.

4.3 Results

The voltage-current (V-I) characteristics of the cell are shown in Fig. 1.

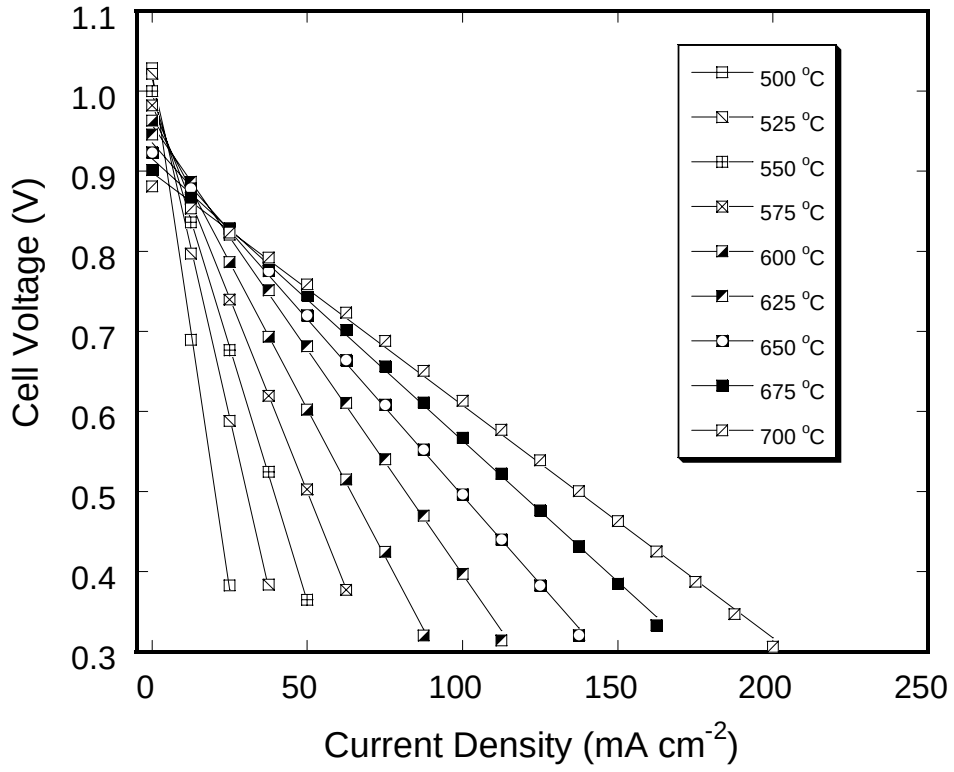


Fig. 1 V-I characteristics of the CGO electrolyte supported solid oxide fuel cell with a PBCO cathode.

As expected for CGO, the open circuit voltages (OCV) (Fig. 2) range from 0.87 V at 700 °C to 1.04V at 500 °C and are lower than Nernst potential. The values for the OCV are comparable to those typically measured with ceria-based electrolytes. The decreased OCV is attributed to the increasing contribution of electronic conductivity to the total conductivity as the temperature is increased in a reducing environment.

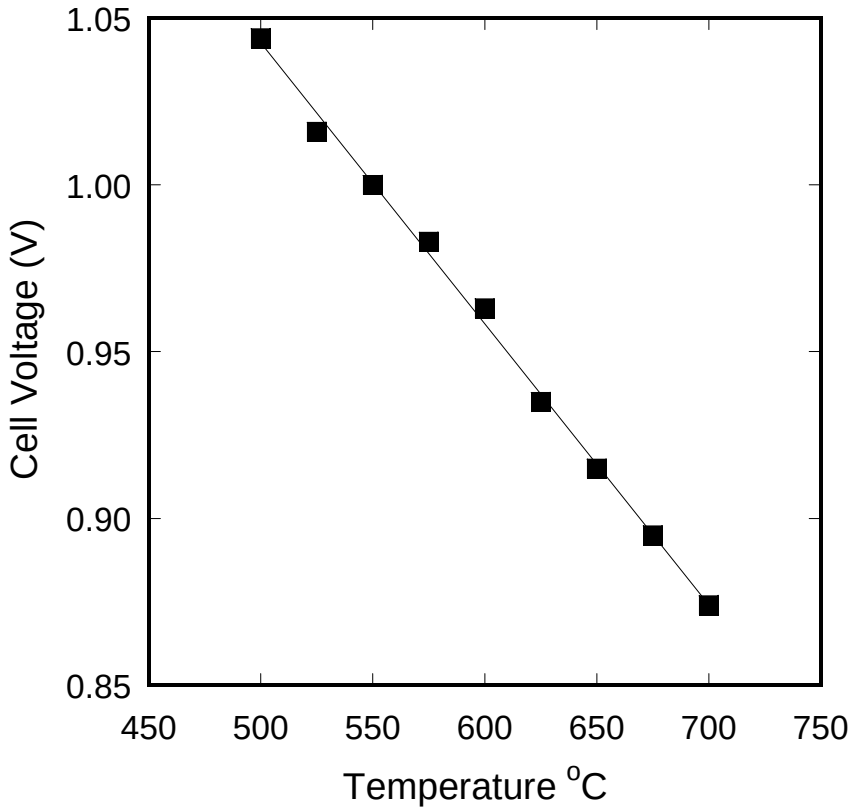


Fig. 2 Open circuit voltages of a CGO/PBCO electrolyte supported solid oxide fuel cell.

The power densities as a function of current density from 500 °C to 700 °C are shown in Fig. 3. The maximum power densities are ranging from 9.6 mW/cm^2 at 500 °C to 69.4 mW/cm^2 at 700 °C. The power densities achievable with this cell are primarily limited by the resistance of the electrolyte. The electrolyte is 0.8 mm thick and contributes the major part of the total cell resistance above 500 °C. The total ohmic resistance of the cell was determined using the current interruption technique. The results are compared with the calculated resistance of CGO using literature data in Fig. 4.

At 700 °C the ohmic resistance of the cell is effectively equal to that of the electrolyte. At 600 °C the difference is small (0.27 ohms) and increases to 5.4 ohms at 500 °C. The present experimental data do not enable the specific electrode contributions to be isolated. Nevertheless at 600 °C the data indicate low electrode resistances.

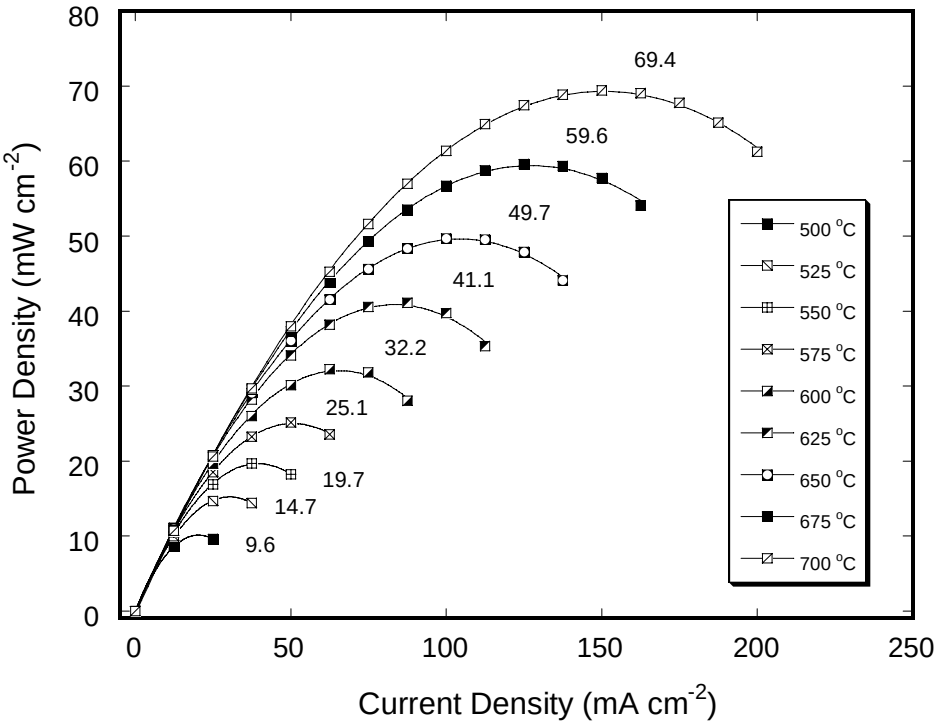


Fig. 3. Power densities of the cell as a function of current density.

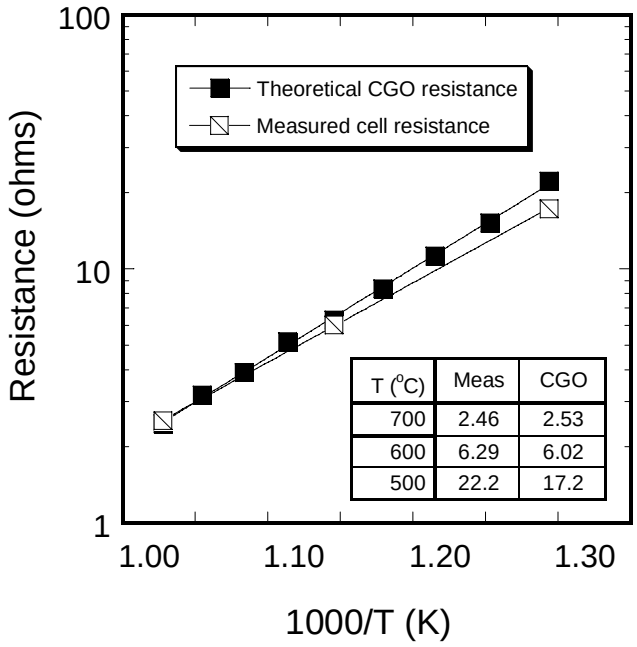


Fig. 4. Comparison of the ohmic resistance of the cell measured by current interrupt technique and the calculated theoretical resistance of the electrolyte.

5. Conclusions

Initial tests of the performance of PBCO as a cathode material were carried out in a complete cell. A composite electrode of PBCO/CGO supported on a thick (0.8 mm) CGO electrolyte. The results as expected are dominated by the electrolyte resistance but at 600 °C, the ohmic resistance of the other components is only ~0.27 ohms. Additional electrode studies are in progress under several different conditions: (1) with a reference electrode on the cathode side to measure directly the cathode contribution to the I-V characteristics, (2) measurements as a function of electrolytes thickness, (3) construction of an anode supported cell. We anticipate that these experiments will provide a final assessment of the potential for PBCO/CGO fuel cells.

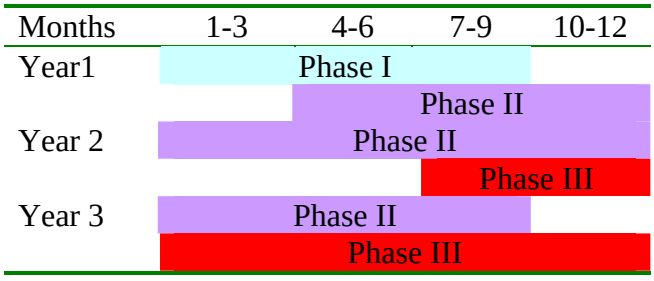
6. References

7. List of Acronyms and Abbreviations

CGO	Cerium Gadolinium Oxide
ECR	Electrical Conductivity Relaxation
EPMA	Electron Probe MicroAnalysis
GDC	Gadolinia Doped Ceria (see CGO)
LSGM	Lanthanum Strontium Magnesium Gallate
PLD	Pulsed Laser Deposition
TGA	Thermogravimetric Analysis
YSZ	Yttria Stabilized Zirconia
IEDP	Isotope Exchange and Depth Profiling
PBCO	Praesodymium Barium Cobalt Oxide
STO	Strontium Titanate
LAO	Lanthanum Aluminate

8. Milestones and Scope of Work

The project is divided into three phases that will overlap as shown in the timelines below



Phase I: The Phase I objectives are to complete the characterization of a set of perovskite materials for which performance data already exists at PNNL. We will then measure the relevant kinetic parameters. The comparison the real performance data with the fundamental kinetic parameters will be used to guide materials selection in Phase II.

Phase II: The Phase II objectives of the project are to synthesize and characterize new cathode materials and to measure their kinetic parameters. The thermal and chemical compatibility with different electrolytes will be determined. Based on these results, a subset of the best materials will be selected for single cell tests. Some additional compositions will be synthesized if indicated by the single cell test data.

Phase III: The phase three objectives are to evaluate the performance of the best materials identified in Phase I and II. The optimum electrode composition and microstructure will be determined and longer term performance characteristics evaluated.

Updated Milestones for Years 1, 2 & 3

PHASE I

Task 1.0	Four modified perovskite oxide compositions (**P1)** selected by UH and PNNL will be synthesized and characterized by X-ray diffraction (XRD) and electron microprobe analysis (EMPA) (Months 6-9) **completed**
Task 2.0	The chemical compatibility with YSZ and CGO electrolytes will be determined (Months 6-9) **completed**
Task 3.0	The temperature dependence of the dc conductivity and stoichiometry will be determined in air for the **P1** compositions. (Months 6-9) **will not be done**
Task 4.0	The diffusion coefficients and surface exchange rates will be measured by electrical conductivity relaxation (Months 6-12) **will not be done**
Task 5.1	Thin films of perovskite compositions will be synthesized by PLD using a combinatorial approach. (Months 3-9) **completed**
Task 5.2	Electrode-electrolyte interfaces will be characterized for thin films of cathode materials by AC impedance spectroscopy (Months 9-12) **completed**
Task 6.0	Electrode-electrolyte interfaces will be characterized for thin films of cathode materials by IEDP (9-12) **completed**

PHASE II

Task 1.0	Four modified perovskite oxide compositions (**P2)** will be synthesized and characterized by XRD and EMPA (Months 9-12) **completed**
Task 1.1	Two A_2BO_4 compositions (**K1)** will be synthesized and characterized by XRD and EMPA. (Months 1-4) **completed**
Task 1.2	Three additional A_2BO_4 compositions (**K2**) will be synthesized and characterized by XRD and EMPA. (Months 6-9) **completed**
Task 2.0	The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for **P2** (Month 12) **completed for YSZ and CGO**
Task 2.1	The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for **K1** (Month 7) **completed for YSZ and CGO**
Task 2.2	The chemical compatibility with YSZ, CGO and LSGM electrolytes will be determined for **K2** (Month 9) **completed for YSZ and CGO**
Task 3.0	The dc conductivity and stoichiometry will be determined in air for the **K1** compositions that have chemical compatibility. (Months 4-6) **completed**

Task 4.0 The diffusion coefficients and surface exchange rates will be measured by electrical conductivity relaxation for the **K1** materials evaluated in Task 3 (Months 6-12). **completed**

Task 4.1 K1 samples will be characterized in symmetric cells by AC impedance spectroscopy (Months 6-9) to confirm the measured values of $k_{ex.}$ **completed**

Task 5.0 Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by AC impedance spectroscopy (Months 10-33).

Task 6.0 Electrode-electrolyte interfaces will be characterized for thin films of cathode materials selected from Task 4.0 by IEDP (Months 10-33) **in completed**

Task 7.0 Results from Tasks 4.0, 5.0, and 6.0 will be used as they become available to select cathode electrolyte combinations for single cell tests (Months 10-33). **in progress**

Phase III

Year 3 Milestones

We have selected three compositions for further study: La_2NiO_4, Pr_2NiO_4, $PrBaCo_2O_{5.5+x}$ in combination with CGO electrolyte. In Phase III we will do the following:

Task 1.1 Fabricate symmetric cells of La_2NiO_4 and measure ASR. **completed**

Task 1.2 Fabricate symmetric cells of $Pr_2NiO_4$and measure ASR. **completed**

Task 1.3 Fabricate symmetric cells of $PrBaCo_2O_{5.5+x}$and measure ASR. **completed**

Task 2.1 Fabricate half cells of La_2NiO_4 and measure electrode resistance by cyclic voltammetry and AC impedance. **completed**

Task 2.2 Fabricate symmetric cells of Pr_2NiO_4 and measure electrode resistance by cyclic voltammetry and AC impedance. **completed**

Task 2.3 Fabricate symmetric cells of $PrBaCo_2O_{5.5+x}$ and measure electrode resistance by cyclic voltammetry and AC impedance. **completed**

Task 3.1 Fabricate single cells with La_2NiO_4 and determine performance.

Task 3.2 Fabricate single cells with Pr_2NiO_4 and determine performance.

Task 3.3 Fabricate single cells with $PrBaCo_2O_{5.5+}$and determine performance. **In progress**